

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
18 October 2001 (18.10.2001)

PCT

(10) International Publication Number
WO 01/77278 A1(51) International Patent Classification⁷: C11D 17/00,
3/14, 1/83, 3/20, 3/04

(21) International Application Number: PCT/US01/10411

(22) International Filing Date: 2 April 2001 (02.04.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/543,916 6 April 2000 (06.04.2000) US(71) Applicant: COLGATE-PALMOLIVE COMPANY
[US/US]; 300 Park Avenue, New York, NY 10022 (US).(72) Inventor: BLANDIAUX, Genevieve; Rue Lonhienne,
3A, B-4870 Trooz (BE).(74) Agent: NANFELDT, Richard, E.; Colgate-Palmolive
Company, 909 River Road, P.O. Box 1343, Piscataway, NJ
08855-1343 (US).(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM,
HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK,
LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX,
MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL,
TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,
IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF,
CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: ACIDIC LIQUID CRYSTAL DETERGENT COMPOSITIONS

(57) Abstract: This invention relates to an acid liquid crystal composition comprising a water insoluble organic compound, a non-ionic surfactant, an abrasive, an anionic surfactant, a cosurfactant, a hydroxy containing organic acid, and water.

WO 01/77278 A1

ACIDIC LIQUID CRYSTAL DETERGENT COMPOSITIONS

Field of the Invention

This invention relates to a liquid crystal detergent composition containing an
5 abrasive and having a pH of 2.7 to 3.8. More specifically, it is of a liquid detergent
composition in liquid crystal state which when brought into contact with oily soil is
superior to other liquid detergent compositions in detergency and in other physical
properties as well as having disinfecting properties.

Background of the Invention

10 Liquid aqueous synthetic organic detergent compositions have long been
employed for human hair shampoos and as dishwashing detergents for hand washing
of dishes (as distinguished from automatic dishwashing machine washing of dishes).
Liquid detergent compositions have also been employed as hard surface cleaners, as
in pine oil liquids, for cleaning floors and walls. More recently they have proven
15 successful as laundry detergents too, apparently because they are convenient to use,
are instantly soluble in wash water, and may be employed in "pre-spotting" applications
to facilitate removals of soils and stains from laundry upon subsequent washing. Liquid
detergent compositions have comprised anionic, cationic and nonionic surface active
agents, builders and adjuvants, including, as adjuvants, lipophilic materials which can
20 act as solvents for lipophilic soils and stains. The various liquid aqueous synthetic
organic detergent compositions mentioned serve to emulsify lipophilic materials,
including oily soils, in aqueous media, such as wash water, by forming micellar
dispersions and emulsions.

Although emulsification is a mechanism of soil removal, it has been only
25 comparatively recently that it was discovered how to make microemulsions which are
much more effective than ordinary emulsions in removing lipophilic materials from
substrates. Such microemulsions are described in British Patent Specification No.
2,190,681 and in U.S. Patents 5,075,026; 5,076,954 and 5,082,584 and 5,108,643,

most of which relate to acidic microemulsions useful for cleaning hard surfaced items, such as bathtubs and sinks which microemulsions are especially effective in removing soap scum and lime scale from them. However, as in Serial No. 4,919,839 the microemulsions may be essentially neutral and such are also taught to be effective for

5 microemulsifying lipophilic soils from substrates. In U.S. Patent application Serial No. 7/313,664 there is described a light duty microemulsion liquid detergent composition which is useful for washing dishes and removing greasy deposits from them in both neat and diluted forms. Such compositions include complexes of anionic and cationic detergents as surface active components of the microemulsions.

10 The various microemulsions referred to include a lipophile, which may be a hydrocarbon, a surfactant, which may be an anionic and/or a nonionic detergent(s), a co-surfactant, which may be a poly-lower alkylene glycol lower alkyl ether, e.g., dipropylene glycol monomethyl ether, and water.

Although the manufacture and use of detergent compositions in microemulsion

15 form significantly improved cleaning power and greasy soil removal, compared to the usual emulsions, the present invention improves them still further and also increases the capacity of the detergent compositions to adhere to surfaces to which they have been applied. Thus, they drop or run substantially less than cleaning compositions of "similar" cleaning power which are in microemulsion or normal liquid detergent form.

20 Also, because they form microemulsions with lipophilic soil or stain material spontaneously, with essentially no requirement for addition of any energy, either thermal or mechanical, they are more effective cleaners at room temperature and at higher and lower temperatures that are normally employed in cleaning operations than are ordinary liquid detergents, and are also more effective than detergent compositions

25 in microemulsion form.

The present liquid crystal detergent compositions may be either clear or somewhat cloudy or milky (opalescent) in appearance but both forms thereof are stable on storage and components thereof do not settle out or become ineffective, even on

storage at somewhat elevated temperatures for periods as long as six months and up to a year. The presence of the cosurfactant in the liquid crystal detergent compositions helps to make such compositions resist freezing at low temperatures.

In accordance with the present invention a liquid detergent composition
5 containing an abrasive, suitable at room temperature or colder, for pre-treating and cleaning materials soiled with lipophilic soil, is in liquid crystal form and comprises synthetic organic surface active agents, a cosurfactant, a solvent for the soil, and water. The invention also relates to processes for treating items and materials soiled with lipophilic soil with compositions of this invention to loosen or remove such soil, by
10 applying to the locus of such soil on such material a soil loosening or removing amount of an invented composition. In another aspect of the invention lipophilic soil is absorbed from the soiled surface into the liquid crystal.

In recent years all-purpose liquid detergents have become widely accepted for cleaning hard surfaces, e.g., painted woodwork and panels, tiled walls, wash bowls,
15 bathtubs, linoleum or tile floors, washable wall paper, etc. Such all-purpose liquids comprise clear and opaque aqueous mixtures of water-soluble synthetic organic

detergents and water-soluble detergent builder salts. In order to achieve comparable cleaning efficiency with granular or powdered all-purpose cleaning compositions, use of water-soluble inorganic phosphate builder salts was favored in the prior art all-purpose
20 liquids. For example, such early phosphate-containing compositions are described in U.S. Patent Nos. 2,560,839; 3,234,138; 3,350,319; and British Patent No. 1,223,739.

In view of the environmentalist's efforts to reduce phosphate levels in ground water, improved all-purpose liquids containing reduced concentrations of inorganic phosphate builder salts or non-phosphate builder salts have appeared. A particularly
25 useful self-opacified liquid of the latter type is described in U.S. Patent No. 4,244,840.

However, these prior art all-purpose liquid detergents containing detergent builder salts or other equivalent tend to leave films, spots or streaks on cleaned

unrinsed surfaces, particularly shiny surfaces. Thus, such liquids require thorough rinsing of the cleaned surfaces which is a time-consuming chore for the user.

In order to overcome the foregoing disadvantage of the prior art all-purpose liquid, U.S. Patent No. 4,017,409 teaches that a mixture of paraffin sulfonate and a
5 reduced concentration of inorganic phosphate builder salt should be employed.

However, such compositions are not completely acceptable from an environmental point of view based upon the phosphate content. On the other hand, another alternative to achieving phosphate-free all-purpose liquids has been to use a major proportion of a mixture of anionic and nonionic detergents with minor amounts of glycol
10 ether solvent and organic amine as shown in U.S. Patent NO. 3,935,130. Again, this approach has not been completely satisfactory and the high levels of organic detergents necessary to achieve cleaning cause foaming which, in turn, leads to the need for thorough rinsing which has been found to be undesirable to today's consumers.

15 Another approach to formulating hard surfaced or all-purpose liquid detergent composition where product homogeneity and clarity are important considerations involves the formation of oil-in-water (o/w) microemulsions which contain one or more surface-active detergent compounds, a water-immiscible solvent (typically a hydrocarbon solvent), water and a "cosurfactant" compound which provides product
20 stability. By definition, an o/w microemulsion is a spontaneously forming colloidal dispersion of "oil" phase particles having a particle size in the range of 25 to 800 Å in a continuous aqueous phase.

In view of the extremely fine particle size of the dispersed oil phase particles, microemulsions are transparent to light and are clear and usually highly stable against
25 phase separation.

Patent disclosures relating to use of grease-removal solvents in o/w microemulsions include, for example, European Patent Applications EP 0137615 and EP 0137616 - Herbots et al; European Patent Application EP 0160762 - Johnston et al;

and U.S. Patent No. 4,561,991 - Herbots et al. Each of these patent disclosures also teaches using at least 5% by weight of grease-removal solvent.

It also is known from British Patent Application GB 2144763A to Herbots et al, published March 13, 1985, that magnesium salts enhance grease-removal performance of organic grease-removal solvents, such as the terpenes, in o/w microemulsion liquid detergent compositions. The compositions of this invention described by Herbots et al. require at least 5% of the mixture of grease-removal solvent and magnesium salt and preferably at least 5% of solvent (which may be a mixture of water-immiscible non-polar solvent with a sparingly soluble slightly polar solvent) and at least 0.1% magnesium salt.

The following representative prior art patents also relate to liquid detergent cleaning compositions in the form of o/w microemulsions: U.S. Patents Nos. 4,472,291 - Rosario; 4,540,448 - Gauteer et al; 3,723,330 - Sheflin; et al.

Liquid detergent compositions which include terpenes, such as d-limonene, or other grease-removal solvent, although not disclosed to be in the form of o/w microemulsions, are the subject matter of the following representative patent

documents: European Patent Application 0080749; British Patent Specification 1,603,047; and U.S. Patent Nos. 4,414,128 and 4,540,505. For example, U.S. Patent No. 4,414,128 broadly discloses an aqueous liquid detergent composition characterized by, by weight:

(a) from 1% to 20% of a synthetic anionic, nonionic, amphoteric or zwitterionic surfactant or mixture thereof;

(b) from 0.5% to 10% of a mono- or sesquiterpene or mixture thereof, at a weight ratio of (a):(b) being in the range of 5:1 to 1:3; and

(c) from 0.5% to 20% of a polar solvent having a solubility in water at 15°C in the range of from 0.2% to 10%. Other ingredients present in the formulations disclosed in this patent include from 0.05% to 10% by weight of an alkali metal, ammonium or alkanolammonium soap of a C₁₃-C₂₄ fatty acid; a calcium sequestrant from 0.5% to

13% by weight; non-aqueous solvent, e.g., alcohols and glycol ethers, up to 10% by weight; and hydrotropes, e.g., urea, ethanolamines, salts of lower alkylaryl sulfonates, up to 10% by weight. All of the formulations shown in the Examples of this patent include relatively large amounts of detergent builder salts which are detrimental to
5 surface shine.

U.S. Patent 5,035,826 teaches liquid crystal compositions but these compositions exhibit thermal stability in the limited temperature range of 19°C to 36°C.

Disinfectant composition based on cationic and nonionic surfactants are well known. However, these compositions while very efficient in disinfecting surfaces,
10 generally do not remove grease and oil as desired; hence, leaving residues and streaks on surfaces. Addition of an efficient anionic surfactant cleaner, to the cationic surfactant, either creates instability problems or deactivates the disinfectant behavior of the cationic. Anionic and nonionic mixtures have a good grease removal properties, but do not perform at all to sanitize the surface being cleaned.

15 Summary of the Invention

The present invention relates to improved, liquid crystal detergent compositions containing an abrasive and having a pH of 2.7 to 3.8, preferably 2.9 to 3.5. The compositions have improved scouring ability and interfacial tension which improves the cleaning of hard surface such as plastic, vitreous and metal surfaces having a shiny
20 finish, oil stained floors, automotive engines and other engines. More particularly, the improved cleaning compositions exhibit good scouring power and grease soil removal properties due to the improved interfacial tensions and leave the cleaned surfaces shiny without the need of or requiring only minimal additional rinsing or wiping. The latter characteristic is evidenced by little or no visible residues on the unrinsed cleaned
25 surfaces and, accordingly, overcomes one of the disadvantages of prior art products.

Surprisingly, these desirable results are accomplished even in the absence of polyphosphate or other inorganic or organic detergent builder salts and also in the complete absence or substantially complete absence of grease-removal solvent.

In one aspect, the invention generally provides a stable, liquid crystal, hard surface cleaning composition especially effective in the removal of oily and greasy oil. The liquid crystal composition includes, on a weight basis:

1% to 30% of a magnesium salt of a C₈-C₁₆ linear alkyl benzene sulfonate

5 surfactant;

1% to 20% of a water-mixable cosurfactant having either limited ability or substantially no ability to dissolve oily or greasy soil;

0.1% to 5% of a magnesium salt such as magnesium oxide, magnesium sulfate heptahydrate or magnesium chloride;

10 0.1% to 10% of a perfume, essential oil, or water insoluble hydrocarbon having 6 to 18 carbon atoms and mixtures thereof;

1% to 20% of at least one ethoxylated nonionic surfactant;

0.1% to 3% of an unsaturated fatty acid having 12 to 20 carbon atoms;

0.01% to 0.5% of an alkali metal hydroxide such as sodium hydroxide or

15 potassium hydroxide;

0.1% to 2% of a hydroxy containing organic acid selecting from the group

consisting of lactic acid, citric acid or the hydroxy benzoic acid and mixtures thereof;

0.01% to 1% of a polymeric thickener such as methacrylate, xanthan gums and hydroxy alkyl celluloses such as hydroxy ethyl cellulose;

20 0.1% to 10% of an abrasive; and

the balance being water, wherein the liquid crystal detergent composition does not contain any grease release agents such as choline chloride or buffering system which is a nitrogenous buffer which is ammonium or alkaline earth carbonate, guanidine derivatives, alkoxylalkyl amines and alkyleneamines C₃-C₇ alkyl and alkenyl
25 monobasic and dibasic acids such as C₄-C₇ aliphatic carboxylic diacids which do not contain a hydroxy group, boric acid, phosphoric acid, amino alkylene phosphonic acid and the composition is pourable and has a storage modulus equal to or higher than one Pascal (1 Newton/sq. m.), more preferably higher than 10 Pascal at a temperature

of 20°C to 40°C at a strain of 0.1% to 5% second as measured on a Carri-Med CS Rheometer and is thermally stable and exist as a clear liquid crystal in the temperature range from 8°C to 43°C, more preferably 4°C to 43°C.

An object of this invention is to provide an antibacterial liquid crystal, hard
5 surface cleaning composition, comprises a zwitterionic surfactant, an abrasive, anionic surfactant and a hydroxy aliphatic acid, wherein the composition does not contain any phosphoric acid, phosphonic acid, boric acid, alkali metal carbonates, alkaline earth metal carbonates, alkyl glycine surfactant or cyclic imidinium surfactant.

Another object of this invention is to provide an antibacterial liquid crystal, hard
10 surface cleaning composition with desirable foam control and cleaning properties which kills bacteria.

Detailed Description of the Invention

The present invention relates to a stable liquid crystal detergent composition comprising approximately by weight: 1% to 30% of a magnesium salt C₈-C₁₆ linear
15 alkyl benzene sulfonate surfactant, 1% to 20% of a cosurfactant, 0.1% to 10%, more preferably 0.4% to 5% of a water insoluble hydrocarbon, essential oil or a perfume,
0.1% to 10% of an abrasive, 0.1% to 2.5% of a fatty acid or an alkali metal salt of a fatty acid, 0.01% to 0.5% of an alkali metal hydroxide such as sodium hydroxide or potassium hydroxide, 0.1% to 2% of a hydroxy containing organic acid such as lactic
20 acid, citric acid and/or the benzoic acid and mixtures thereof, 1% to 20% of at least ethoxylated nonionic surfactant, 0.01% to 1% of a polymeric thickener such as methacrylate, xanthan gums and hydroxy alkyl celluloses such as hydroxy ethyl cellulose and the balance being water, wherein the liquid detergent composition does not contain any grease release agents such as choline chloride or buffering system
25 which is a nitrogerious buffer which is ammonium or alkaline earth carbonate, guanidine derivates, alkoxyalkyl amines and alkyleneamines C₃-C₇ alkyl and alkenyl monobasic and dibasic acids such as C₄-C₇ aliphatic carboxylic diacids which do not contain a hydroxy group, boric acid, phosphoric acid, amino alkylene phosphonic acid

and the composition has a storage modulus equal to or higher than one Pascal (1 Newton/sq. m.), more preferably higher than 10 Pascal at a temperature of 20°C to 40°C at a strain of 0.1% to 5% second as measured on a Carri-Med CS Rheometer and is thermally stable and exist as a liquid crystal in the temperature range from 10°C to 45°C, more preferably 4°C to 43°C.

According to the present invention, the role of the water insoluble hydrocarbon can be provided by a non-water-soluble perfume. Typically, in aqueous based compositions the presence of a solubilizers, such as alkali metal lower alkyl aryl sulfonate hydrotrope, triethanolamine, urea, etc., is required for perfume dissolution, especially at perfume levels of 1% and higher, since perfumes are generally a mixture of fragrant essential oils and aromatic compounds which are generally not water-soluble.

As used herein and in the appended claims the term "perfume" is used in its ordinary sense to refer to and include any non-water soluble fragrant substance or mixture of substances including natural (i.e., obtained by extraction of flower, herb, blossom or plant), artificial (i.e., mixture of natural oils or oil constituents) and synthetically produced substance) odoriferous substances. Typically, perfumes are complex mixtures of blends of various organic compounds such as alcohols, aldehydes, ethers, aromatic compounds and varying amounts of essential oils (e.g., terpenes) such as from 0% to 80%, usually from 10% to 70% by weight, the essential oils themselves being volatile odoriferous compounds and also serving to dissolve the other components of the perfume.

Quite surprisingly although the perfume is not, per se, a solvent for greasy or oily soil, --even though some perfumes may, in fact, contain as much as 80% of terpenes which are known as good grease solvents -- the inventive compositions in dilute form have the capacity to solubilize up to 10 times or more of the weight of the perfume of oily and greasy soil, which is removed or loosened from the hard surface by virtue of

the action of the anionic and nonionic surfactants, said soil being taken up into the oil phase of the o/w microemulsion.

In the present invention the precise composition of the perfume is of no particular consequence to cleaning performance so long as it meets the criteria of water immiscibility and having a pleasing odor. Naturally, of course, especially for
5 cleaning compositions intended for use in the home, the perfume, as well as all other ingredients, should be cosmetically acceptable, i.e., non-toxic, hypoallergenic, etc.

The hydrocarbon such as a perfume is present in the liquid crystal composition in an amount of from 0.6% to 10% by weight, preferably from 0.8% to 8% by weight,
10 especially preferably from 1% to 6% by weight. If the amount of hydrocarbon (perfume) is less than 0.6% by weight it becomes difficult to form the liquid crystal. If the hydrocarbon (perfume) is added in amounts more than 10% by weight, the cost is increased without any additional cleaning benefit and, in fact, with some diminishing of cleaning performance insofar as the total amount of greasy or oily soil which can be
15 taken up in the oil phase of the microemulsion will decrease proportionately.

Furthermore, although superior grease removal performance will be achieved for perfume compositions not containing any terpene solvents, it is apparently difficult for
perfumers to formulate sufficiently inexpensive perfume compositions for products of this type (i.e., very cost sensitive consumer-type products) which includes less than
20 20%, usually less than 30%, of such terpene solvents.

Thus, merely as a practical matter, based on economic consideration, the liquid crystal cleaning compositions of the present invention may often include as much as 0.2% to 7% by weight, based on the total composition, of terpene solvents introduced thereunto via the perfume component. However, even when the amount of terpene
25 solvent in the cleaning formulation is less than 1.5% by weight, such as up to 0.6% by weight or 0.4% by weight or less, satisfactory grease removal and oil removal capacity is provided by the inventive compositions.

In place of the perfume in either the microemulsion composition or the all purpose hard surface cleaning composition at the same previously defined concentrations that the perfume was used in either the microemulsion or the all purpose hard surface cleaning composition one can employ an essential oil or a water insoluble organic compound such as a water insoluble hydrocarbon having 6 to 18 carbon such as a paraffin or isoparaffin such as isoparH, isodecane, alpha-pinene, beta-pinene, decanol and terpeneol.

Suitable essential oils are selected from the group consisting of: Anethole 20/21 natural, Aniseed oil china star, Aniseed oil globe brand, Balsam (Peru), Basil oil (India), Black pepper oil, Black pepper oleoresin 40/20, Bois de Rose (Brazil) FOB, Borneol Flakes (China), Camphor oil, White, Camphor powder synthetic technical, Cananga oil (Java), Cardamom oil, Cassia oil (China), Cedarwood oil (China) BP, Cinnamon bark oil, Cinnamon leaf oil, Citronella oil, Clove bud oil, Clove leaf, Coriander (Russia), Coumarin 69°C (China), Cyclamen Aldehyde, Diphenyl oxide, Ethyl vanilin, Eucalyptol, Eucalyptus oil, Eucalyptus citriodora, Fennel oil, Geranium oil, Ginger oil, Ginger oleoresin (India), White grapefruit oil, Guaiacwood oil, Gurjun balsam, Heliotropin, Isobornyl acetate, Isolongifolene, Juniper berry oil, L-methyl acetate, Lavender oil, Lemon oil, Lemongrass oil, Lime oil distilled, Litsea Cubeba oil, Longifolene, Menthol crystals, Methyl cedryl ketone, Methyl chavicol, Methyl salicylate, Musk ambrette, Musk ketone, Musk xylol, Nutmeg oil, Orange oil, Patchouli oil, Peppermint oil, Phenyl ethyl alcohol, Pimento berry oil, Pimento leaf oil, Rosalin, Sandalwood oil, Sandenol, Sage oil, Clary sage, Sassafras oil, Spearmint oil, Spike lavender, Tagetes, Tea tree oil, Vanilin, Vetyver oil (Java), Wintergreen

The at least one nonionic surfactant is present in amounts of about 1% to 20%, preferably 2% to 16% by weight of the liquid crystal composition and provides superior performance in the removal of oily soil and mildness to human skin.

The water soluble ethoxylated nonionic surfactants utilized in this invention are commercially well known and include the primary aliphatic alcohol ethoxylates and

secondary aliphatic alcohol ethoxylates. The length of the polyethenoxy chain can be adjusted to achieve the desired balance between the hydrophobic and hydrophilic elements.

The nonionic surfactant class includes the condensation products of a higher
5 alcohol (e.g., an alkanol containing about 8 to 16 carbon atoms in a straight or branched chain configuration) condensed with about 4 to 20 moles of ethylene oxide, for example, lauryl or myristyl alcohol condensed with about 16 moles of ethylene oxide (EO), tridecanol condensed with about 6 to moles of EO, myristyl alcohol condensed with about 10 moles of EO per mole of myristyl alcohol, the condensation product of
10 EO with a cut of coconut fatty alcohol containing a mixture of fatty alcohols with alkyl chains varying from 10 to about 14 carbon atoms in length and wherein the condensate contains either about 6 moles of EO per mole of total alcohol or about 9 moles of EO per mole of alcohol and tallow alcohol ethoxylates containing 6 EO to 11 EO per mole of alcohol.

15 A preferred group of the foregoing nonionic surfactants are the Neodol ethoxylates (Shell Co.), which are higher aliphatic, primary alcohol containing about 9-15 carbon atoms, such as C₉-C₁₁ alkanol condensed with 4 to 10 moles of ethylene oxide (Neodol 91-8 or Neodol 91-5), C₁₂₋₁₃ alkanol condensed with 6.5 moles ethylene oxide (Neodol 23-6.5), C₁₂₋₁₅ alkanol condensed with 12 moles ethylene
20 oxide (Neodol 25-12), C₁₄₋₁₅ alkanol condensed with 13 moles ethylene oxide (Neodol 45-13), and the like. Such ethoxamers have an HLB (hydrophobic lipophilic balance) value of about 8 to 15 and give good O/W emulsification, whereas ethoxamers with HLB values below 7 contain less than 4 ethyleneoxide groups and tend to be poor emulsifiers and poor detergents.

25 Additional satisfactory water soluble alcohol ethylene oxide condensates are the condensation products of a secondary aliphatic alcohol containing 8 to 18 carbon atoms in a straight or branched chain configuration condensed with 5 to 30 moles of ethylene oxide. Examples of commercially available nonionic detergents of the

foregoing type are C₁₁-C₁₅ secondary alkanol condensed with either 9 EO (Tergitol 15-S-9) or 12 EO (Tergitol 15-S-12) marketed by Union Carbide.

The anionic sulfonate surfactants which may be used in the detergent of this invention are water soluble and include the sodium, potassium, ammonium and
5 ethanolammonium salts of linear C₈-C₁₆ alkyl benzene sulfonates; C₈-C₁₈ alkyl sulfates and mixtures thereof. The preferred anionic sulfonate surfactant is a magnesium salt of a C₈-C₁₆ linear alkyl benzene sulfonate surfactant.

Examples of sulfonated anionic detergents are the well known higher alkyl mononuclear aromatic sulfonates, such as the higher alkylbenzene sulfonates
10 containing 9 to 18 or preferably 9 to 16 carbon atoms in the higher alkyl group in a straight or branched chain, or C₈-15 alkyl toluene sulfonates. A preferred alkylbenzene sulfonate is a linear alkylbenzene sulfonate having a higher content of 3-phenyl (or higher) isomers and a correspondingly lower content (well below 50%) of 2-phenyl (or lower) isomers, such as those sulfonates wherein the benzene ring is attached mostly
15 at the 3 or higher (for example 4, 5, 6 or 7) position of the alkyl group and the content of the isomers in which the benzene ring is attached in the 2 or 1 position is correspondingly low. Preferred materials are set forth in U.S. Patent 3,320,174, especially those in which the alkyls are of 10 to 13 carbon atoms.

The major class of compounds found to provide highly suitable cosurfactants for
20 the microemulsion over temperature ranges extending from 5°C to 43°C for instance are glycerol, ethylene glycol, water-soluble polyethylene glycols having a molecular weight of 300 to 1000, polypropylene glycol of the formula HO(CH₂CHCH₂O)_nH wherein n is a number from 2 to 18, mixtures of polyethylene glycol and polypropyl glycol (Synalox) and mono C₁-C₆ alkyl ethers and esters of ethylene glycol and
25 propylene glycol having the structural formulas R(X)_nOH and R₁(X)_nOH wherein R is C₁-C₆ alkyl group, R₁ is C₂-C₄ acyl group, X is (OCH₂CH₂) or (OCH₂(CH₃)CH) and n is a number from 1 to 4, diethylene glycol, triethylene glycol, an alkyl lactate, wherein

the alkyl group has 1 to 6 carbon atoms, 1methoxy-2-propanol, 1methoxy-3-propanol, and 1methoxy 2-, 3- or 4-butanol.

Representative members of the polypropylene glycol include dipropylene glycol and polypropylene glycol having a molecular weight of 200 to 1000, e.g., polypropylene glycol 400. Other satisfactory glycol ethers are ethylene glycol monobutyl ether (butyl cellosolve), diethylene glycol monobutyl ether (butyl carbitol), triethylene glycol monobutyl ether, mono, di, tri propylene glycol monobutyl ether, tetraethylene glycol monobutyl ether, mono, di, tripropylene glycol monomethyl ether, propylene glycol monomethyl ether, ethylene glycol monohexyl ether, diethylene glycol monohexyl ether, propylene glycol tertiary butyl ether, ethylene glycol monoethyl ether, ethylene glycol monomethyl ether, ethylene glycol monopropyl ether, ethylene glycol monopentyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monopropyl ether, diethylene glycol monopentyl ether, triethylene glycol monomethyl ether, triethylene glycol monoethyl ether, triethylene glycol monopropyl ether, triethylene glycol monopentyl ether, triethylene glycol monohexyl ether, mono, di, tripropylene glycol monoethyl ether, mono, di tripropylene glycol monopropyl ether, mono, di, tripropylene glycol monopentyl ether, mono, di, tripropylene glycol monohexyl ether, mono, di, tributylene glycol mono methyl ether, mono, di, tributylene glycol monoethyl ether, mono, di, tributylene glycol monopropyl ether, mono, di, tributylene glycol monobutyl ether, mono, di, tributylene glycol monopentyl ether and mono, di, tributylene glycol monohexyl ether, ethylene glycol monoacetate and dipropylene glycol propionate. Tripropylene glycol n-butyl ether is the preferred cosurfactant because of its hydrophobic character.

The amount of cosurfactant required to stabilize the liquid crystal compositions will, of course, depend on such factors as the surface tension characteristics of the cosurfactant, the type and amounts of the primary surfactants and perfumes, and the type and amounts of any other additional ingredients which may be present in the composition and which have an influence on the thermodynamic factors enumerated

above. Generally, amounts of cosurfactant used in the liquid crystal composition is in the range of from 1% to 20%, preferably from 2% to 12% by weight provide stable dilute liquid crystal composition for the above-described levels of primary surfactants and perfume and any other additional ingredients as described below.

- 5 The instant liquid crystal compositions contain about 0.1 to 10 wt. %, more preferably 0.25 to 2.0 wt. % of an abrasive selected from the group consisting of amorphous hydrated silica and polyethylene powder particles and mixtures thereof.

 The amorphous silica (oral grade) used to enhance the scouring ability of the liquid crystal gel was provided by Zeoffin. The mean particles size of Zeoffin silica is
10 about 8 up to about 10 mm. Its apparent density is about 0.32 to about 0.37 g/ml. Another amorphous silica from Rhone-Poulenc is Tixosil 103 having a mean particle size of 8 to 12 μ m and an apparent density of 0.25-0.4 g/ml. An amorphous hydrated silica from Crossfield of different particles sizes (9, 15 and 300 mm), and same apparent density can also be used. The polyethylene powder used in the instant
15 invention as an abrasive has a particle size of about 200 to about 500 microns and a density of about 0.91 to about 0.99 g/liter, more preferably about 0.94 to about 0.96.

 The instant composition contains about 0.1 to about 5 wt. %, more preferably about 0.25 to about 3 wt. % of a magnesium salt such as magnesium chloride, magnesium oxide and/or magnesium sulfate heptahydrate and mixtures thereof.

- 20 The cleaning compositions can include from 0.1 to 3.0 wt. %, preferably from 0.2 wt. % to 2.5 wt. %, of the composition of a C₈-C₂₂ fatty acid or fatty acid soap as a foam suppressant. The addition of fatty acid or fatty acid soap provides an improvement in the rinseability of the composition whether applied in neat or diluted form. Generally, however, it is necessary to increase the level of cosurfactant to
25 maintain product stability, when the fatty acid or soap is present. If more than 2.5 wt. % of a fatty acid is used in the instant compositions, the composition will become unstable at low temperatures as well as having an objectionable smell.

The final essential ingredient in the inventive microemulsion compositions having improved interfacial tension properties is water. The proportion of water in the liquid crystal detergent composition generally is in the range of 20% to 97%, preferably 70% to 97% by weight.

5 The liquid cleaning composition of this invention may, if desired, also contain other components either to provide additional effect or to make the product more attractive to the consumer. The following are mentioned by way of example: Colors or dyes in amounts up to 0.5% by weight; bactericides in amounts up to 1% by weight; preservatives or antioxidizing agents, such as formalin, 5-bromo-5-nitro-dioxan-1,3; 5-
10 chloro-2-methyl-4-isothallazolin-3-one, 2,6-di-tert.butyl-p-cresol, etc., in amounts up to 2% by weight; and pH adjusting agents, such as sulfuric acid or sodium hydroxide, as needed. Furthermore, if opaque compositions are desired, up to 4% by weight of an opacifier may be added.

A composition of this invention is in a liquid crystal state when it is of lyotropic
15 structure, is transparent or slightly turbid (opalescent) but not opaque, and has a storage modulus equal to or higher than one Pascal (1 Newton/sq. m.), more preferably higher than 10 Pascal and most preferably higher than 20 Pascal and when measured
at a temperature of 20 to 40°C, at a frequency of ten radians per second and at a strain of 0.1 to 5%. The rheological behavior of the compositions of this invention were
20 measured at 25°C by means of a Carri-Med CS Rheometer. In making the measurement, a cone and plate are used at a cone angle of 2 degrees: 0 minutes: 0 seconds with a cone diameter of 6.0 cm, measurement system gap of 52.0 micro m and a measurement system inertia of 17.02 micro Nm sec⁻². The liquid crystal compositions have a pH of about 2.7 to about 5.0, more preferably 2.9 to 4.0.

25 To make the liquid crystal compositions of the invention is relatively simple because they tend to form spontaneously with little need for the addition of energy to promote transformation to the liquid crystal state. However, to promote uniformity of the composition mixing will normally be undertaken and it has been found desirable first

to mix the surfactants and cosurfactant with the water, followed by admixing of the lipophilic component, usually a hydrocarbon (but esters or mixtures of hydrocarbons and esters may also be employed). It is not necessary to employ heat and most mixings are preferably carried out at about room temperature (20-25°C).

5 The invented compositions may be applied to such surfaces by pouring onto them, by application with a cloth or sponge, or by various other contacting means but it is preferred to apply them in the form of a spray by spraying them onto the substrate from a hand or finger pressure operated sprayer or squeeze bottle. Such application may be onto hard surfaces, such as dishes, walls or floors, from which lipophilic
10 (usually greasy or oily) soil is to be removed, or may be onto fabrics, such as laundry, which has previously been stained with lipophilic soils, such as motor oil. The invented compositions may be used as detergents and as such may be employed in the same manner in which liquid detergents are normally utilized in dishwashing, floor and wall cleaning and laundering, but it is preferred that they be employed as pre-spotting
15 agents too, in which applications they are found to be extremely useful in loosening the adhesions of lipophilic soils to substrates, thereby promoting much easier cleaning with application of more of the same invented detergent compositions or by applications of different commercial detergent compositions, in liquid, bar or particulate forms.

20 The various advantages of the invention have already been set forth in some detail and will not be repeated here. However, it will be reiterated that the invention relates to the important discovery that effective liquid detergent compositions can be made in the liquid crystal state and that because they are in such state they are especially effective in removing lipophilic soils from substrates and also are effective in removing from substrates non-lipophilic materials. Such desirable properties of the
25 liquid crystal detergent compositions of this invention make them ideal for use as pre-spotting agents and detergents for them ideal for use as pre-spotting agents and detergents for removing hard-to-remove soils from substrates in various hard and soft surface cleaning operations.

The following examples illustrate but do not limit the invention. Unless otherwise indicated, all parts in these examples, in the specification and in the appended claims are by weight and all temperature are in °C.

Example I

5 The following formulas (wt. %) were made at 25°C by simple mixing.

	A	B	C
C10-C14 linear alkyl benzene sulfonate	11.44	11.44	11.44
C9-C11 alcohol EO 2.5:1 nonionic	1.9	1.9	1.9
C9-C11 alcohol EO 5:1 nonionic	1.9	1.9	1.9
Magnesium oxide	0.69	0.69	0.69
Tixosil 103 - amorphous silicon	1.1	1.1	1.1
Coconut fatty acid	1.0	1.0	1.0
NaOH	0.23	0.23	0.23
Lactic acid	0.625	0.625	0.625
Natrosol 250 HHBR (hydroxy ethyl cellulose)	0.05	0.1	0.05
Perfume	0.5	0.5	0.5
Isopar H (isoparaffin)	0.95	0.95	0.95
Dipropylene glycol monobutyl ether	5.7	5.7	5.7
pH	3.5	3.5	3.0
EN 1276 bacterial test	Passed		

Formulas A, B and C were tested against a commercial cream scourer for soap scum removal and Formulas A-C were rated better than the commercial cream scourer.

~~10 The invention has been described with respect to various embodiments and~~

illustrations of it but is not to be considered as limited to these because it is evident that one of skill in the art with the present specification before him or her will be able to utilize substitutes and equivalents without departing from the invention.

What is Claimed is:

1. A liquid crystal detergent composition which comprises by weight:
 - (a) about 1% to about 20% of at least one nonionic surfactant containing ethylene oxide groups;
 - 5 (b) 1% to 30% of a magnesium salt of a C₈-C₁₆ linear alkyl benzene sulfonate surfactant;
 - (c) about 0.1% to about 10% of an abrasive;
 - (d) about 1% to about 20% of a cosurfactant;
 - (e) about 0.1% to about 10% of a water insoluble organic compound selected
 - 10 from the group consisting of perfumes, essential oils and water insoluble hydrocarbons having about 8 to about 18 carbon atoms;
 - (f) 0.1% to 5% of a magnesium salt;
 - (g) 0.1% to 3% of a fatty acid and/or alkali metal salt of a fatty acid;
 - (h) 0.1% to 2% of a hydroxy containing organic acid;
 - 15 (i) 0.01% to 1% of a polymeric thickener; and
 - (j) the balance being water, said liquid crystal detergent composition has a

pH of 2.7 to 3.8 and a storage modulus measured at a temperature between 20°C to 40°C, at a strain of 0.1% to 5% and a frequency of 10 radians/second of at least about one Pascal and is one phase at a temperature of 8°C to 43°C.
- 20 2. The composition of Claim 1, wherein at least one of said nonionic surfactant is a condensation product of one mole of a higher fatty alcohol having about 9 to about 11 carbon atoms with 2 to 6 moles of said ethylene oxide groups.
3. The composition of Claim 2, wherein said cosurfactant is dipropylene glycol n-butyl ether.
- 25 4. The composition of Claim 1, wherein said abrasive is selected from the group consisting of amorphous hydrated silica or polyethylene powder and mixtures thereof.

5. The composition of Claim 1 wherein said hydroxy containing organic acid is selected from the group consisting of lactic acid, citric acid and ortho hydroxy benzoic acid and mixtures thereof.

6. The composition of Claim 5 wherein said polymeric thickener is hydroxy
5 ethyl cellulose.

7. The composition of Claim 6 wherein said magnesium salt is magnesium oxide.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/10411

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C11D17/00 C11D3/14 C11D1/83 C11D3/20 C11D3/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 97 32968 A (COLGATE PALMOLIVE CO) 12 September 1997 (1997-09-12) claims; example 1	1,2,5
A	US 5 849 105 A (BLANDIAUX GENEVIEVE ET AL) 15 December 1998 (1998-12-15) claims	1,2,4
A	US 5 922 666 A (BLANDIAUX GENEVIEVE) 13 July 1999 (1999-07-13) claims; examples	1,2,4
A	WO 97 47726 A (COLGATE PALMOLIVE CO) 18 December 1997 (1997-12-18) claims	1,2,4

-/--

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *Z* document member of the same patent family

Date of the actual completion of the international search

21 August 2001

Date of mailing of the international search report

29/08/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Grittern, A

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/10411

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 958 856 A (BLANDIAUX GENEVIEVE ET AL) 28 September 1999 (1999-09-28) claims; example 1 -----	1,2,4

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/10411

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9732968 A	12-09-1997	AU 711740 B	21-10-1999
		AU 2212197 A	22-09-1997
		CA 2247902 A	12-09-1997
		EP 0885290 A	23-12-1998
		NZ 331726 A	28-01-1999
		PL 328696 A	15-02-1999
		US 5958852 A	28-09-1999
US 5849105 A	15-12-1998	AU 713425 B	02-12-1999
		AU 3384397 A	07-01-1998
		BG 103017 A	30-09-1999
		EP 0906411 A	07-04-1999
		HU 9903434 A	28-03-2000
		PL 330641 A	24-05-1999
		WO 9747726 A	18-12-1997
US 5922666 A	13-07-1999	AU 6521399 A	15-05-2000
		WO 0024855 A	04-05-2000
WO 9747726 A	18-12-1997	AU 713425 B	02-12-1999
		AU 3384397 A	07-01-1998
		BG 103017 A	30-09-1999
		EP 0906411 A	07-04-1999
		HU 9903434 A	28-03-2000
		PL 330641 A	24-05-1999
		US 5849105 A	15-12-1998
US 5958856 A	28-09-1999	US 5523013 A	04-06-1996
		US 5035826 A	30-07-1991
		AU 711075 B	07-10-1999
		AU 2321897 A	22-09-1997
		CA 2247816 A	12-09-1997
		EP 0888447 A	07-01-1999
		NZ 331724 A	30-08-1999
		PL 328708 A	15-02-1999
		WO 9732966 A	12-09-1997
		US 5741770 A	21-04-1998
		US 5958852 A	28-09-1999
		US 5707957 A	13-01-1998
		US 5723431 A	03-03-1998
		US 5898026 A	27-04-1999
		AT 145936 T	15-12-1996
		AU 630232 B	22-10-1992
		AU 6304090 A	28-03-1991
		CA 2025956 A	23-03-1991
		DD 295865 A	14-11-1991
		DE 69029306 D	16-01-1997
		DE 69029306 T	03-07-1997
		DK 418986 T	26-05-1997
		EP 0418986 A	27-03-1991
		ES 2097132 T	01-04-1997
		GR 90100712 A,B	20-01-1992
		HU 212246 B	29-04-1996
		IE 903417 A	10-04-1991
		JP 3207799 A	11-09-1991
		KR 165853 B	15-12-1998
		NO 177908 B	04-09-1995
		NZ 235408 A	25-11-1992

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☒ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.